

*Application No. 10/044337**Amendment  
Page 4***REMARKS**

Reconsideration of the Official Action of August 6, 2003 is requested.

*Specification*

The specification has been objected to for several informalities, which have all been addressed above. The new paragraph added at page 9, between lines 19 and 20 provides the requested antecedent specification support for claims 2 and 18.

*Drawings*

Fig. 6B of the drawings has been objected to as including reference numeral 78, without corresponding text. Item 78 has been deleted from the Figure on the enclosed corrected drawing page.

*Double Patenting*

Claims 1, 3-17 and 19-50 have been rejected for double patenting over claims 1, 3-17, and 19-50 of Trozerra, US 5,902,475, taken with Anderson et al, US 6,391,502; and claims 2 and 18 have been rejected for double patenting over Trozerra, taken with Anderson et al as applied to claims 1 and 17, and further in view of Lucas et al (EP 078485).

A machine translation of the text of EP 078485 has been prepared and a copy is enclosed for the examiner's information.

Trozerra is commonly owned. Therefore, to advance prosecution a terminal disclaimer is filed herewith to remove Trozerra as a reference for double patenting. The applicant does not acquiesce in the rejection by filing the terminal disclaimer.

*Conclusion*

The specification and drawing objections have been addressed and double patenting rejection has been obviated. The application is believed to be in condition for allowance. Early and favorable action thereon is requested.

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Respectfully submitted,

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# EP0780485 A1

Method and apparatus for cleaning a metal substrate

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## Abstract

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A metal substrate cleaning process comprises: creating a plasma in a mixture of hydrogen, hydrogen compounds and/or inert gas (e.g. argon) to generate radicals and/or ions for acting on the substrate which is negatively biased with respect to an anode facing the surface to be cleaned. Also claimed is a metal substrate cleaning apparatus, especially for carrying out the above process, comprising devices for generating a plasma and negatively biasing the substrate surface.

*Alta Vista translation from <http://12.espacenet.com/espacenet/viewer?PN=EP0780485>*

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## Description

The present invention relates to a process for the scouring of a metal substrate, such as a sheet steel, in particular for the elimination of a layer of contamination, so as to support the adhesion of a coating applied later on to this substrate.

In general, according to the techniques currently applied, one makes use of a chemical agent of scouring to clean metal surfaces, such as sheets, before the application of a coating. Such techniques present in particular the disadvantage of requiring a putting into circulation of relatively significant quantities of generally harmful agents of scouring for which it is necessary to envisage a process of regeneration to allow their recycling.

One of the essential goals of this invention is to cure this disadvantage and of more than present a very effective process with a great output of scouring.

To this end, the process following the invention consists in creating near the surface of the substrate to clean a plasma in a mixture of hydrogen, compounds hydrogenated and/or of an inert gas, such as argon, so as to generate radicals and/or ions forming of the excited species, this substrate being negatively polarized compared to an anode arranged compared to surface to clean thus allowing the above mentioned radicals and/or ions to act on this surface.

Advantageously, one makes use of a magnetic circuit laid out on the side of the substrate opposed to surface to clean of this last.

According to a particular embodiment of the invention, in order to allow obtaining a continuous process, one makes ravel the substrate compared to the above mentioned magnetic circuit.

The invention also relates to a device in particular allowing the implementation of the above mentioned process. This device is characterized by the fact that it includes/understands a) a vacuum enclosure, b) of the means making it possible to create in this enclosure a plasma, as c) of the means making it possible to polarize surface negatively to be cleaned of a substrate introduced into the aforesaid enclosure compared to an anode arranged compared to this surface.

Other details and characteristics of the invention will arise from the description given hereafter as an example nonrestrictive, particular embodiment of the process and device following the invention with reference to the figures.

Figure 1 is a representation in the form of graphics the speed of scouring in Angström (ANGSTRÖM) a second according to the pressure and composition of the gaseous medium in which scouring takes place.

Figure 2 represents a graph showing the evolution of the water vapor concentration in the gaseous medium according to the pressure and the composition

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of the gaseous medium in which scouring takes place.

Figure 3 is a diagrammatic representation of a transverse section of a particular embodiment of the device, according to the invention, for the cleaning of a metal substrate.

The invention relates to a process for the scouring of a metal substrate, more particularly a sheet steel, for its later covering by a coating. In general, such sheets, outgoing of the rolling mills, present surface layers of contamination, such as oxides, which have a harmful effect on adhesion of a coating applied later on to this sheet, for example, by electrolysis or immersion in a molten metal bath.

The process following the invention consists in fact to apply the known technique of cathode sputtering to surface to be cleaned of a metal substrate.

Thus, according to this process one creates, near this surface, polarized negatively compared to an anode arranged compared to the latter, a plasma in a mixture of hydrogen, compounds hydrogenated and/or one of an inert gas, such as argon, so as to generate radicals and/or ions allowing to act on surface to be cleaned. They are more particularly species excited in a cold plasma with low pressure of about 0,001 to 10 Torr.

This plasma is maintained near the surface of the substrate by means of a magnetic circuit of containment of the electrons, which is thus advantageously laid out near this surface behind the substrate, i.e. side opposed to that where plasma is formed.

In order to make it possible to obtain a continuous process, surface to be treated and the magnetic circuit are in relative displacement one compared to the other.

In an advantageous configuration, the substrate ravel in front of the magnetic circuit, this last being thus in this case maintained in a motionless position.

The hydrogenated radicals produced in the discharge of plasma make it possible to eliminate by reduction metallic oxides in the form of vapor from water, while the formed carbonaceous derivatives are eliminated in the form from hydrocarbon compounds. When this mixture contains an inert gas, in particular of argon, the action of scouring is carried out mainly by ionic bombardment. This mechanical effect makes it possible to activate surface to be cleaned while eliminating, on the one hand, of the adsorbed water molecules coming from the oxidation of the radicals of hydrogen and, on the other hand, oxides or derivatives carbonaceous.

In a particularly advantageous embodiment of the invention, the magnetic circuit is of type cd. magnetron, i.e. with D.C. current, and surface to be cleaned is maintained with the mass.

When the substrate is made of an appreciably continuous sheet, the latter moves compared to the magnetic circuit, for example at a speed of about 100 to 500 m/min, preferably about 400 m/min.

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As into the traditional processes of cathode sputtering, the inert gas is introduced into the plasma 2 formed in enclosure 1 by injectors 11 directed towards the metal coil 4.

The range of pressures of the above mentioned gas mixture can advantageously vary from 1 Torr, for a gas containing 100 % of hydrogen and/or hydrogenated compounds, with 0,005 Torr, for a gas containing 100 % of an inert gas, the intermediate pressures corresponding to intermediate mixtures of hydrogen and/or compounds hydrogenated with inert gas with relationship between hydrogen and/or the hydrogenated compounds with respect to decreasing inert gases in an appreciably continuous way for decreasing pressures in the same proportions.

The scouring of a soft sheet steel can be explained by three principal mechanisms in a argon-hydrogen mixture:

the reduction of the surface layer in FeO, generally a thickness of 5 Nm, steels by the hydrogen activated in plasma

according to the total reaction  $\text{FeO} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O}$ , and

the pulverization of the surface layer in FeO by the argon ions, and

the pulverization of iron by the argon ions.

In this respect, it is necessary to notice that the value the speed of erosion of FeO is generally about half of that of iron in cathode sputtering to 100 % of argon.

If the layer of contamination is made of iron oxide, the essential reactions intervening for its removal can in fact of being written as follows:

$\text{H}_2 \rightarrow 2\text{H}$

$\text{Ar} \rightarrow \text{Ar} + \text{E}$

$\text{FeO} + 2\text{H} \rightarrow \text{Fe} + \text{H}_2\text{O}$   $\text{Fe} + \text{Ar} +$

$\text{E} \rightarrow \text{Ar} + \text{Fe}$

Experiments were led in order to optimize the conditions of scouring, i.e. to increase the kinetics of scouring.

They made it possible to distinguish, according to the invention, two particularly interesting fields: a field of scouring to low pressure (pressure < 5.10 Torr, to see fig. 1) and a field of scouring to high pressure (pressure > 5.10 Torr, to also see fig. 1).

More particularly, figure 1 fact of appearing clearly that there is to work in the presence of hydrogen

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and with the lowest possible pressure in the mode called to low pressure P ranging between 2.10 Torr and 5.10 Torr, whereas there is to work with the highest possible pressure in the mode called to high pressure. In this respect it is necessary to note that the pressure must be higher than 0.17 Torr if one wants to exceed the maximum speed of scouring which one can reach in mode low pressure.

Figure 1 is built starting from kinetic equations of scouring empirically established according to the pressure and of the gas mix design. In this figure like in figure 2, curve "A" refers to an atmosphere of pure hydrogen, the curve "B" with an atmosphere containing 80 % of hydrogen and 20 % of argon, while the curve "C", in figure 2, relates to an atmosphere of pure argon.

In the case of an atmosphere of argon, the maximum speed of scouring is given by the following equation:

$$^{(1)} v = -13^{\circ} P^{\circ} Dp + 1,2^{\circ} Dp$$

in which:

v: speed of scouring (ANGSTRÖM/S)

P: total pressure (Torr)

Dp: density of power (W/cm)

the operation range is as follows:

$$2.10 \text{ Torr} < P < 0,1 \text{ Torr}$$

Below 2.10 Torr, the formation of a plasma magnetron is not practically possible any more, whereas above 0,1 Torr the thermalisation of the argon ions in gas becomes sufficiently significant so that the speed of scouring with pure argon falls to zero.

In the case of an atmosphere of hydrogen, the maximum speed of scouring is given by the following equation:

$$^{(2)} v = 14,3^{\circ} P^{\circ} Dp$$

When one is in the presence of pure hydrogen the field of stability of the discharge corresponds to pressures ranging between 10 Torr and 100 Torr.

If one adds more than 20 % of argon in the mixture, the lower limit of the field of stability of plasma passes from 10 Torr to 2.10 Torr. In this respect, it is necessary to note that argon stabilizes the discharge with low pressure.

In the case of a mixed atmosphere of argon and hydrogen (with more than 20 % of argon in the mixture), the maximum speed of scouring is given by the following equation:

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$$^{(3)} v = -25^{\circ} P^{\circ} Dp + 2,4^{\circ} Dp$$

For a field of stability of plasma identical to that of an atmosphere of pure argon, it is necessary that the pressure lies between 2.10 Torr and 0,1 Torr for a minimum hydrogen flow fixed by the following equation:

$$^{(4)} QH_2 = 22,4^{\circ} L^{\circ} I^{\circ} v$$

in which:

L: working length of the zone of scouring (m)

I: bandwidth (m)

v: speed of scouring (ANGSTRÖM/S)

and for a concentration out of hydrogen lower or equal to 80 %. Au-tops of 80 % out of hydrogen, the quantity of iron pulverized by argon decreases and one tends towards the case of the process to high pressure out of hydrogen slower than the process to low pressure when the pressure is lower than 0.17 Torr.

Indeed, the water content in the phase vapor is always lower for the process than low pressure compared to the process with high pressure.

Consequently, the process with low pressure must be selected if the hydrogen flows are limited and also if one does not make use of traps, for example a trap to liquid nitrogen, to decrease the water content in the phase vapor. Indeed, with low pressure, the iron pulverized by the argon ions, which settle on a shielding of recovery located opposite the zone of scouring (by assumption of surface equivalent to the surface of the pickled zone) reoxyde immediately in contact with the water vapor.

This reoxidation of pulverized iron makes it possible to eliminate the vapor from water which is not then available any more for the reoxidation of pickled sheet. It is obviously not the case when there is no pulverization of iron by argon, i.e. with high pressure. In such a case, one must imperatively decrease the water content in the phase vapor by increasing the gas output, particularly out of hydrogen, and/or placing traps, such as cold walls, to condense water.

It results consequently from what precedes that for a pressure P by the gaseous medium in the enclosure of scouring lower than 5.10 Torr, i.e. in a mode with low pressure, optimal scouring is obtained by the use of a pumping installation dimensioned in manner such as "P" can vary from 2.10 Torr with 5.10 Torr, and is preferably about 5.10 Torr to have a stable plasma. In addition, it is necessary that the hydrogen flow "QH2", sufficient to appreciably

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reduce all the layer of FeO presents at the surface of the metal coil to pickle, answers the  $QH_2 > 22,4 \cdot L \cdot v$  relation (see equation 4) at the speed of acceptable maximum line and that the argon flow is fixed so that the hydrogen content is lower than 80 %. In this respect, it is generally indicated to work between 20 and 50 % of hydrogen. It is important to note that, under these working conditions, the pickled sheet is generally not sensitive to a strong recontamination by the water produced at the time of the reduction of FeO by hydrogen. Indeed, water reoxyde immediately the iron pulverized on the shielding of the device used facing the zone of scouring.

For a pressure P of the gaseous medium in the enclosure of scouring higher than 5.10 Torr, i.e. in a mode called "high pressure", optimal scouring is obtained by the use of a pumping installation dimensioned in manner such as P varies from 0,17 Torr with 50 Torr, and is preferably about 1 Torr so that the speed of scouring exceeds the maximum value obtained in the above definite embodiment of the process following the invention, called "mode low pressure".

In addition, it is necessary that, like already mentioned above, the sufficient hydrogen flow "QH<sub>2</sub>" to appreciably reduce all the layer of FeO present at the surface of the metal coil to pickle, answers the same relation as in the embodiment called "mode with low pressure". Contrary to what is the case for the preceding embodiment, the embodiment called "mode with high pressure" is quite sensitive to the recontamination of the strip pickled by the water produced at the time of the reduction of Fe by hydrogen. In order to decrease this recontamination, one can, like also already mentioned above, increase the gas output and possibly place traps, for example in the form of cold walls, to condense the formed steam.

The two embodiments described above are more illustrated for the two concrete examples taken again hereafter.

#### Example 1

It acts of an example carried out in the mode with low pressure

VL (speed of line) = 150 m/min.

L (length of traitement/face) = 2 m

l (length of band) = 1 m

Dp = 26 W/cm

mixes: Ar + H<sub>2</sub>

P = 5.10 Torr

Speed of scouring = 60 ÅNGSTRÖM /s minimum

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Débit of hydrogen: 2600 sccm

Flow of argon: 3000 sccm Concentration out of water: SIMILAR 2 %Vol.H<sub>2</sub>O

#### Example 2

This example relates to the mode high pressure.

VL: 150 m/min

Dp = 26 W/cm

P: 1 Torr

V: 14,3.Dp.P

For Dp: 26 W/cm<sup>2</sup>

V: 372 ÅNGSTRÖM /s

L = 0,33 m l = 1 m.

QH<sub>2</sub> min. = 2750 sccm

The water concentration is a function of the total flow and the presence of cold walls. Without cold walls, with a total flow (Ar + H<sub>2</sub>) = 27500 sccm, the water content in gas was 10 %.

In these examples "sccm" means "Standard cubic centimeter per minute" with "Standard" corresponding to the working conditions of 1 atmosphere to 298 K Ains, 1 sccm is equal to 1,27.10 Torr.P/seconde or 4,46.10 molécules/seconde

Figure 3 shows a particular embodiment of a device for the implementation of the process as described above and applied to a metal coil moving in an appreciably continuous way in glance of a magnetic circuit.

This device includes/understands an enclosure vacuum 1, means, generally known while oneself, making it possible to create in this enclosure 1 a plasma 2, and means making it possible to polarize surface negatively to clean 3 of a metal coil 4, forming the substrate, compared to an anode 5 arranged compared to this surface 3.

A magnetic circuit 6 is arranged side opposite of surface to clean 3 of band 4 compared to anode 5.

In this particular embodiment, the metal coil 4 is applied, with its surface to clean 3 directed towards outside, against a part of the cylindrical wall of a hollow drum 7 turning around its axis 8 in the direction of arrow 9, so as to involve this band 4 following a continuous

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translatory movement in the direction of arrow 10.

The magnetic circuit 6 is assembled in a motionless way inside drum 7, near the cylindrical wall of this last and compared to the part of this wall against which band 4 is applied. If necessary, this drum 7 can be cooled internally on the level of the magnetic circuit, for example with water. Such means of cooling however were not represented on figure 3.

The magnetic circuit 6 consists of a succession of magnets, laid out alternatively northern "N" and southern "S", as shown on figure 3, and the drum even is negatively polarized. This one is preferably carried out in a nonferromagnetic material.

According to a particular case of the invention, drum 7 and, consequently, the metal coil 4 moving on this last can be put at the mass, while the walls of enclosure 1 can be put at a floating potential.

Hereafter is given a concrete example of the application of this device for the scouring of a soft sheet steel, whose surface to clean 3 presents a layer of 5 Nm thickness of iron oxide.

This sheet is involved in enclosure 1 of a device, by drum 7 put in rotation around its axis 8, so as to apply to sheet a speed of line of about 400 m/min. Dimensions of enclosure 1 are such as the length of the zone of treatment of sheet 4 in the direction of the displacement of the latter on drum 7 is about 2 m, so that the processing time corresponds to 0,3 second.

It was noted that, in the device shown on figure 3, the oxide coating which is present on the surface of sheet can be eliminated, in a mixture of argon and hydrogen with low pressure, by maintaining with this sheet a density of power of 40 W/cm.

It is clearly understood that the invention is not limited to this particular form of the invention and that many alternatives can be considered without leaving the framework of this invention.

Thus, in certain cases, the metal coil 4 can move according to a rectilinear motion, for example above a plane support, below which the magnetic circuit is assembled. The process can be appropriate to remove very varied layers of contamination since, especially by the ions of inert gas, this removal can take place only one mechanical manner. The thickness of the layer of contamination can for example vary between 1 and 50 Nm, in particular if this one primarily consists of iron oxide. Also mechanical, known means in oneself, can be designed to evacuate the removed particles of contamination of the metal coil.

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##### Claims

1. Process for the scouring of a metal substrate, characterized in that it consists in creating near the surface of the substrate to pickle a plasma in a mixture of hydrogen, compounds hydrogenated and/or of an inert gas, such as argon, so as to generate radicals and/or ions, this substrate being negatively polarized compared to an anode arranged compared to surface to pickle thus allowing the radicals and/or ions to act on the latter.
2. Process following claim 1, characterized in that one does use of a magnetic circuit laid out on the side of the substrate opposed to surface to pickle of the latter.
3. Process according to the claim 1 or 2, characterized in that one subjects above mentioned surface and the magnetic circuit to a relative displacement one compared to the other.
4. Process according to claim 3, characterized in that one makes ravel the substrate compared to the above mentioned magnetic circuit.
5. Process according to any of claims 2 to 4, characterized in that one feeds the magnetic circuit by a D.C. current.
6. Process following any of claims 1 to 5, characterized in that one does use of a formed substrate of an appreciably continuous sheet moving compared to the magnetic circuit, for example at a speed of about 300 to 500 m/min, preferably about 400 m/min.
7. Process according to any of claims 1 to 6, characterized in that one carries out plasma with a pressure from 0,001 to 10 Torr of the radicals and/or ions formed.
8. Process according to any of claims 1 to 7, characterized in that one carries out varying scouring in the above mentioned mixture with a pressure of 0,1 Torr for 100 % of hydrogen and/or hydrogenated compounds with 0,005 Torr for 100 % of an inert gas, the intermediate pressures corresponding to intermediate mixtures of hydrogen and/or compounds hydrogenated with inert gas.
9. Process according to any of claims 1 to 7, characterized in that above mentioned surface to pickle is ground connection.
10. Device for the scouring of a metal substrate, in particular for the implementation of the process following any of claims 1 to 9, characterized in that it includes/understands a vacuum enclosure (1), means allowing to create in this enclosure a plasma (2), as of the means allowing to polarize surface negatively to be pickled of a substrate (4) introduced into the aforesaid enclosure (1) compared to an anode (5) arranged compared to this surface.
- 11 Device following claim 10, characterized in that it includes/understands a magnetic circuit (6) arranged on the side opposite of surface to pickle (3) of the substrate (4) compared to the above mentioned anode (5).
12. Device according to claim 11, characterized in that the substrate (4) being formed by a band moving in the above mentioned enclosure (1), it includes/und rstands a hollow drum (7) turning around its axis (8), of the means being designed to apply this band against part of its cylindrical wall so as to involve it according to a translatory movement, the above mentioned

magnetic circuit (6) being gone up in a motionless way inside the drum (7) near this cylindrical wall and compared to the part of the latter against which the band (4) is applied.

13 Device following claim 12, characterized in that the drum (7) is made out of a nonferromagnetic material.

14 Device following any of claims 10 to 13, characterized in that means are designed to maintain the substrate (4) with the mass.

15 Device following any of claims 10 to 14, characterized in that means are designed to put the walls of the enclosure (1) at a floating potential.